Final Report

Biomark/Organic Analysis with Time-of-Flight Mass Spectrometry

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to NASA/Goddard NAG5-12171

Performance Characteristics of the Comprehensive 2-Dimensional Gas Chromatography (GCxGC) Coupled with Time-of-Flight Mass Spectrometry (TOFMS) at the University of Michigan

The report covers the NASA/Goddard award NAG5-12171 and describes the accomplishments from inception until April 2004.

The GC x GC Breadboard Systems

The concept of a GCxGC-TOFMS for the analysis of organic compounds has been proven with commercially available instrumentation (LECO Corp). The performance of a GCxGC instrument has been characterized in various stages using two independent breadboard systems. The GCxGC separation systems, including the thermal modulator, have been miniaturized to the size of a benchtop configuration. One breadboard system employs a Flame Ionization Detector (FID), whereas the second breadboard system employs a Time-of-Fight mass spectrometer (TOFMS) as a detection system (see photograph in Figure 1).

The TOFMS employs an electron impact ion source with orthogonal extraction and a grid-less reflectron for single reflection operation in a flight-representative envelope. Both systems consist of a modular arrangement of individual subunits and use a liquid-sample injection port. This configuration allows for easy replacement of next-generation subunits to the brassboard level.

A limit of detection (LOD) better than 200 ppt for octane has been demonstrated with the breadboard system equipped with the FID detector and an air-cooled thermal modulator. This value has been determined by analyzing an analytical standard covering a linear range from 1 ppb to 1 ppm. The limit of detection has been derived using the slope of the logarithmic value of the integrated area (volume) versus the logarithmic value of the concentration (mass) and the standard deviation of a blank by extrapolating the linear calibration graph to 3 times the signal-to-noise (S/N) ratio. A linear response covering more than 3 orders of magnitude has been demonstrated, as shown in Figure 2.

Using the prototype thermal modulator that incorporates a closed liquid cooling loop and

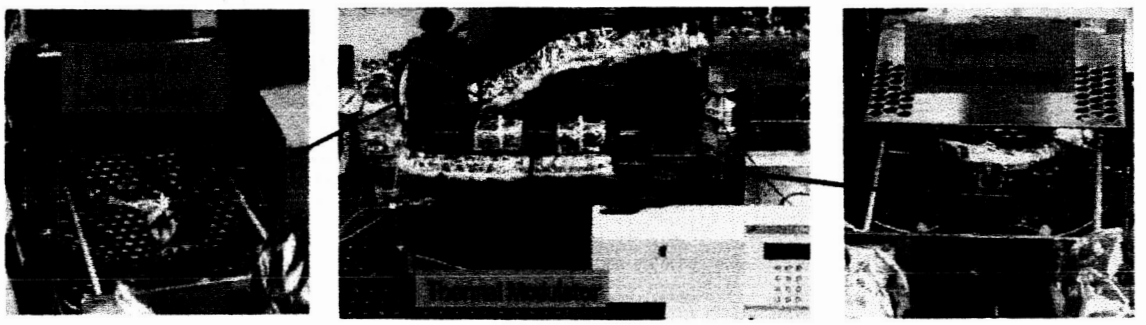

Figure 1: The photograph shows the 2DGC-TOFMS breadboard with the thermal modulator at the connection of both column as well as the TOFMS system used for the data acquisition (center picture). The pictures on the right and left show the wrapped columns including the heating and temperature-control devices.

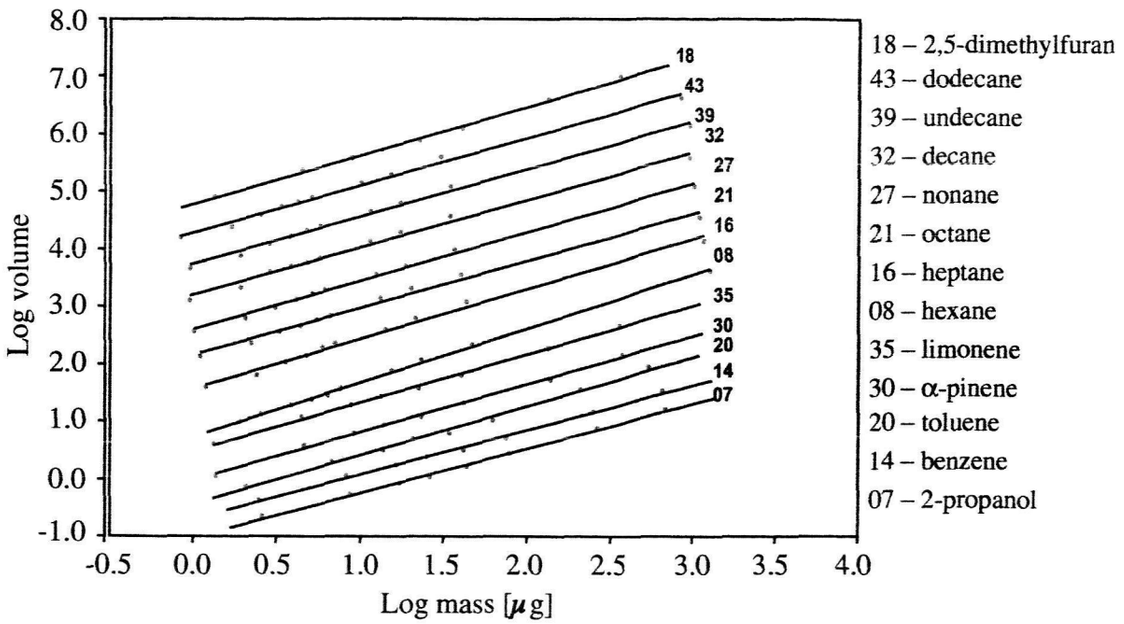

Figure 2: Linear response of the 2DGC breadboard system using an analytical standard covers more than 4 orders of magnitude.

rapid resistive heating (about 100 ms), efficient trapping has been demonstrated. The sample plugs injected into the second column result in peak widths well below 80 ms at the 50% level. A 1-ppm octane standard was analyzed by the breadboard GCxGC-FID system. Calculating the S/N at this concentration and then solving for the required mass needed to produce a signal 3 times the S/N produced a limit of detection of 110 pg/μl, corresponding to 110 ppt.

A LOD lower than 100 pg/μl (corresponding to 100 ppt) for octane has been measured for the breadboard system with the TOFMS system. This result is based on the orthogonal extraction ion source with one extracted ion per extraction pulse firing. With the proposed storage ion source we will be able to inject about 1000 times the number of ions compared to the ions from an orthogonal extraction ion source, and therefore achieve a detection limit in the low ppt range. This extrapolation is justified by the published sensitivity value for the commercial LECO TOFMS system which uses a storage ion source and claims a detection limit of 2 pg/μl. A qualitative data set for a gasoline sample using the GCxGC breadboard system with the FID is shown in Figure 3.

The modulated detector response displayed in the 2-dimensional retention plane allows the complexity of the gasoline sample to be visualized in a more systematic manner (see Figure 3).

The performance of the breadboard 2DGC system with a Time-of-Flight mass spectrometer is shown in Figure 4. The TOFMS system operates in a single reflection survey mode with moderate resolution (500 at full width half maximum) covering a mass range up to 100 amu for a sample mixture of different carbon compounds diluted in acetone. The mass spectra sample rate is 20 kHz and the total ion current (TIC) of the chromatogram has been taken every 100 ms, accumulating 2000 individual mass spectra.

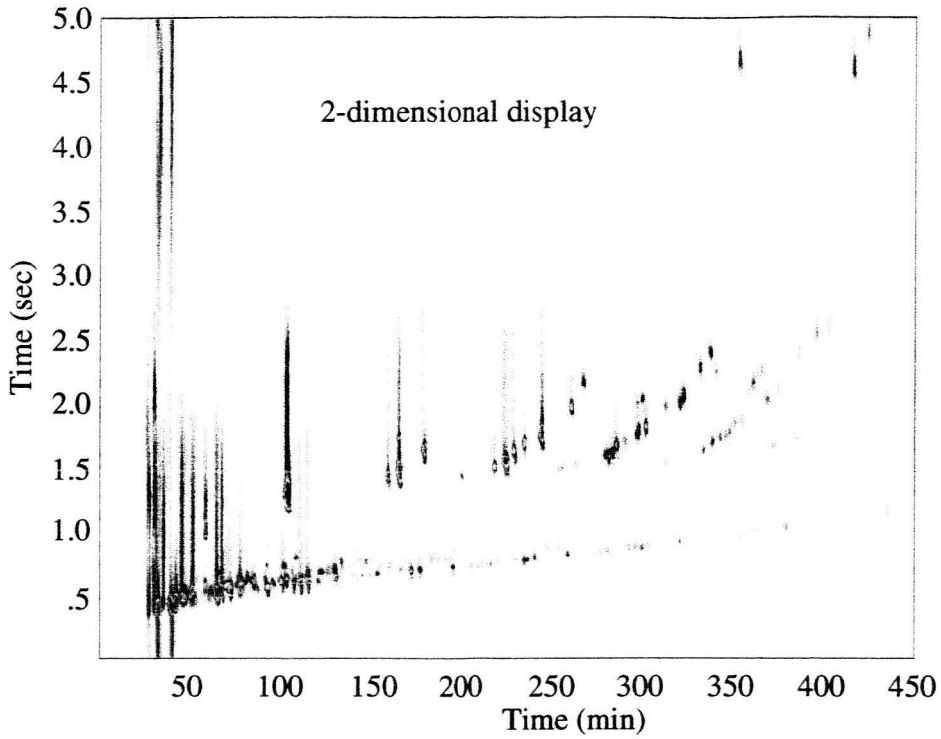

Figure 3: The graph shows a 2-D display of a gasoline sample taken with the 2DGC breadboard system.

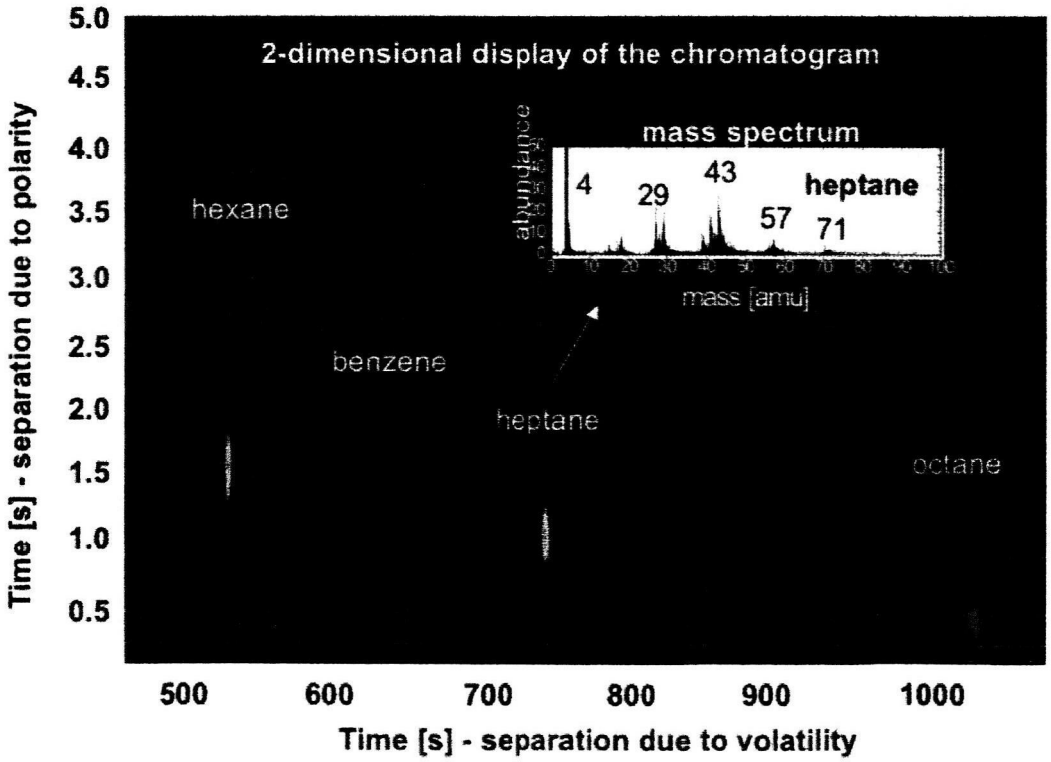

Figure 4: The chromatogram presents a basic carbon sample mixture diluted in acetone displayed in the 2-D retention plane with the corresponding mass spectrum of the heptane peak as an insertion.

PUBLICATIONS

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